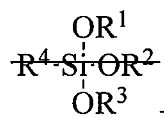
This listing of claims will replace all prior versions, and listings, of claims in the application:

Listing of Claims:

1. (Currently amended) A method of preparing bimodal meso/macroporous siliceous materials comprising combining an organic polyol silane precursor with one or more additives under conditions suitable for hydrolysis and condensation of the precursor to a siliceous material and for phase separation to occur before gelation, wherein the one or more additives are ~~selected from~~ one or more water-soluble polymers and ~~one or more trifunctional silanes of Formula I:~~



~~I~~

~~wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide Si-OH groups; and R^4 is group that is not hydrolyzed under normal sol-gel conditions,~~ wherein the conditions ~~suitable for hydrolysis and condensation of the precursor to a siliceous material~~ comprise combining the organic polyol silane precursor with the one or more additives at a pH in the range of about 4 to 10 ~~about 11.5~~.

2. (Original) The method according to claim 1, wherein the one or more additives are water soluble polymers selected from one or more of polyethers, polyalcohols, polysaccharides, poly(vinyl pyridine), polyacids, polyacrylamides and polyallylamine.

3. (Original) The method according to claim 2, wherein the one or more additives are water soluble polymers selected from one or more of polyethylene oxide (PEO), polyethylene glycol (PEG), amino-terminated polyethylene oxide (PEO-NH_2), amino-terminated polyethylene glycol (PEG-NH_2), polypropylene glycol (PPG), polypropylene

oxide (PPO), polypropylene glycol bis(2-amino-propyl ether) ($PPG-NH_2$), polyvinyl alcohol, poly(acrylic acid), poly(vinyl pyridine), poly(N-isopropylacrylamide) (polyNIPAM) and polyallylamine (PAM).

4. (Original) The method according to claim 3, wherein the one or more additives are water soluble polymers selected from one or more of PEO, $PEO-NH_2$, PEG, $PPG-NH_2$, polyNIPAM and PAM.

5. (Original) The method according to claim 3, wherein the one or more additives are water soluble polymers selected from one or more of PEO, $PEO-NH_2$ and polyNIPAM.

6. (Original) The method according to claim 1, wherein the one or more additives is a mixture of water soluble polymers,

7. (Original) The method according to claim 6 wherein the mixture of water soluble polymers comprises PEO and $PEO-NH_2$.

8. (Original) The method according to claim 5, wherein the one or more additives is PEO.

9. (Original) The method according to claim 8, wherein the PEO has a molecular weight that is greater than about 10,000 g/mol.

10. (Original) The method according to claim 9, wherein the PEO is used at a concentration of greater than about 0.005 g/mL of final solution.

11. (Original) The method according to claim 5, wherein the one or more additives is $PEO-NH_2$.

12. (Original) The method according to claim 11, wherein the PEO-NH_2 has a molecular weight that is greater than about 3,000 g/mol and is used at a concentration of about 0.005 g/mL of final solution.

13. (Original) The method according to claim 5, wherein the one or more additives is poly(N-isopropylacrylamide).

14. (Original) The method according to claim 13, wherein the poly(N-isopropylacrylamide) has a molecular weight that is about 10,000 g/mol and is used at a concentration of about 0.005 g/mL of final solution.

15. – 36. (Cancelled herein)

37. (Original) The method according to claim 1, wherein the organic polyol silane precursor is selected from the group consisting of diglycerylsilane (DGS), monosorbitylsilane (MSS), monomaltosylsilane (MMS), dimaltosylsilane (DMS) and dextran-based silane (DS).

38. (Currently amended) The method according to claim 1, wherein the conditions ~~suitable for the hydrolysis and condensation of the precursor to a siliceous material~~ comprise combining the organic polyol silane precursor with the one or more additives in aqueous solutions and with optional sonication to assist in dissolution.

39. (Previously amended) A method of preparing siliceous materials with low shrinkage characteristics comprising:

(a) combining an aqueous solution of one or more compounds of Formula I:

$$R^4\text{-}\overset{\displaystyle OR^1}{\underset{\displaystyle OR^3}{Si}}\text{-}OR^2 \qquad \text{I},$$

wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide Si-OH groups; and R^4 is group

that is not hydrolyzed under normal sol-gel conditions, with an aqueous solution of an organic polyol silane precursor;

(b) adjusting the pH of the solution in (a) to about 4-11.5;

(c) allowing the solution of (b) to gel;

(d) aging the gel of (c); and

(e) drying the aged gel in air.

40. (Original) A siliceous material prepared using the method according to claim 1.

41. (Currently amended) A method of preparing monolithic bimodal meso/macroporous silica materials comprising combining an organic polyol silane precursor with one or more additives selected from one or more water-soluble polymers and one or more compounds of Formula I:

$$\begin{array}{c} OR^1 \\ | \\ R^4\text{-}Si\text{-}OR^2 \\ | \\ OR^3 \end{array} \qquad \text{I},$$

wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide Si-OH groups, R^4 is group selected from polymer-(linker)$_n$- and

$$\begin{array}{c} OR^1 \\ | \\ R^2O{-}Si{-}(\text{linker})_n{-}\text{polymer}{-}(\text{linker})_n{-} \\ | \\ OR^3 \end{array}$$

and n = 0-1, under conditions suitable for hydrolysis and condensation of the precursor to a siliceous material and for ~~where a~~ phase transition to occur~~s~~ before gelation, wherein the conditions ~~where a phase transition occurs before gelation~~ comprise combining the organic polyol silane precursor with the one or more additives at a pH in the range of about 4 to 10 ~~about 11.5~~.

42. (Original) The method according to claim 41, wherein R^4 is

$$\begin{array}{c} OR^1 \\ | \\ R^2O{-}Si{-}(\text{linker})_n{-}\text{polymer}{-}(\text{linker})_n{-} \\ | \\ OR^3 \end{array}.$$

43. (Original) The method according to claim 42, wherein the linker group is a C_{1-4}alkylene group and n is 1.

44. (Original) The method according to claim 42, wherein OR^1, OR^2 and OR^3 are the same and are selected from C_{1-4}alkoxy.

45. (Original) The method according to claim 42, wherein the polymer is PEO.

46. (Original) The method according to claim 41 wherein the compound of Formula I is selected from the group consisting of:
$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~4-5, average MW 200 (Compound **5a**);
$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~13, average MW 600 (Compound **5b**);
$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~44, average MW 2000 (Compound **5c**); and
$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~227, average MW 10,000 (Compound **5d**).

47. (Original) The method according to claim 41, wherein the water soluble polymer is selected from one or more of PEO, PEO-NH_2 and poly(NIPAM).

48. (Original) A meso/macroporous silica monolith prepared using the method according to claim 41.

49.-53. (Cancelled herein)

54. (Currently amended) A method of preparing a <u>bimodal meso/macroporous</u> monolithic silica chromatographic column comprising placing a solution comprising an organic polyol silane precursor and one or more additives selected from one or more water-soluble polymers and one or more compounds of Formula I:

$$\begin{array}{c} OR^1 \\ R^4\text{-}\overset{|}{\underset{|}{Si}}\text{-}OR^2 \\ OR^3 \end{array} \qquad \text{I,}$$

wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide a Si-OH group; R^4 is group selected from polymer-(linker)$_n$- and

$$\begin{array}{c} OR^1 \\ R^2O-\overset{|}{\underset{|}{Si}}-(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ OR^3 \end{array}$$

and n = 0-1, in a column under conditions suitable for hydrolysis and condensation of the precursor to a siliceous material and for ~~a~~ phase transition to occur before gelation, wherein the conditions ~~suitable for a phase transition to occur before gelation~~ comprise combining the organic polyol silane precursor with the one or more additives at a pH in the range of about 4 to 10 ~~about 11.5~~.

55. (Previously amended) The method according to claim 54, wherein the solution further comprises one or more substances, which provide cationic sites that counterbalance an anionic charge of the silica to reduce non-selective interactions

56. (Currently amended) A chromatographic column comprising a bimodal meso/macroporous silica monolith prepared by combining an organic polyol silane precursor and one or more additives selected from one or more water-soluble polymers and one or more compounds of Formula I:

$$\begin{array}{c} OR^1 \\ R^4\text{-}\overset{|}{\underset{|}{Si}}\text{-}OR^2 \\ OR^3 \end{array} \qquad \text{I,}$$

wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide Si-OH groups; R^4 is group selected from polymer-(linker)$_n$- and

$$\begin{array}{c} OR^1 \\ R^2O-\overset{|}{\underset{|}{Si}}-(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ OR^3 \end{array}$$

and n = 0-1, under conditions suitable for hydrolysis and condensation of the precursor to a siliceous material and for ~~where a~~ phase transition to occur~~s~~ before gelation, wherein the conditions ~~suitable for a phase transition to occur before gelation~~ comprise combining the organic polyol silane precursor with the one or more additives at a pH in the range of about 4 to 10 ~~about 11.5~~.

57. (Currently amended) A method of preparing a bimodal meso/macroporous silica column having an active biomolecule entrapped therein comprising combining:

a) a polyol-silane derived silica precursor;

b) one or more additives selected from one or more water soluble polymers and one or more compounds of Formula I:

$$\begin{array}{c} OR^1 \\ R^4\text{-}\underset{|}{\overset{|}{Si}}\text{-}OR^2 \\ OR^3 \end{array} \qquad \text{I,}$$

wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide Si-OH groups, R^4 is group selected from polymer-$(\text{linker})_n$- and

$$\begin{array}{c} OR^1 \\ R^2O-\underset{|}{\overset{|}{Si}}—(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ OR^3 \end{array}$$

and n is 0-1; and

c) a biomolecule;

under conditions suitable for hydrolysis and condensation of the precursor to a siliceous material and for ~~wherein a~~ phase separation to occur~~s~~ before gelation, wherein the conditions ~~suitable for a phase transition to occur before gelation~~ comprise combining the organic polyol silane precursor with the one or more additives at a pH in the range of about 4 to 10 ~~about 11.5.~~

58. (Original) The method according to claim 57, wherein the one or more additives is one or more water soluble polymers or one or more compounds of Formula I, wherein R^4 is

$$\begin{array}{c} OR^1 \\ R^2O-\underset{|}{\overset{|}{Si}}—(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ OR^3 \end{array}.$$

59. (Previously amended) The method according to claim 57, wherein the organic polyol silane silica precursor, one or more additives and biomolecules are also combined with a substance which provides cationic sites that counterbalance an anionic charge of the silica to reduce non-selective interactions.

60. (Original) A chromatographic column prepared using a method according to claim 57.

61. (Original) A method of performing immunoaffinity chromatography, sample cleanup, solid phase extraction or preconcentration of analytes, removal of unwanted contaminants, solid phase catalysis or frontal affinity chromatography comprising:

(a) applying a sample to a column according to claim 60: and

(b) performing immunoaffinity chromatography, sample cleanup, solid phase extraction or preconcentration of analytes, removal of unwanted contaminants, solid phase catalysis or frontal affinity chromatography.

62. (Previously amended) A method of preparing siliceous materials with enhanced protein stabilizing ability comprising combining an organic polyol silane precursor with one or more additives under conditions suitable for hydrolysis and condensation of precursor to a siliceous material, wherein the one or more additives is selected from one or more trifunctional silanes of Formula I:

$$R^4\text{-}\underset{\displaystyle OR^3}{\overset{\displaystyle OR^1}{Si}}\text{-}OR^2 \qquad \mathbf{I}$$

wherein wherein OR^1, OR^2 and OR^3 are the same or different and represent a group that is hydrolyzed under normal sol-gel conditions to provide a Si-OH group and R^4 is polyol-(linker)-.

63. (Previously amended) The method according to claim 62, wherein the polyol in R^4 is derived from sugar alcohols, sugar acids, saccharides, oligosaccharides or polysaccharides.

64. (Original) The method according to claim 63, wherein the polyol in R^4 is derived from allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose, threose, erythrose, glyceraldehydes, sorbose, fructose,

dextrose, levulose, sorbitol, sucrose, maltose, cellobiose, lactose, dextran (500-50,000 MW), amylose, pectin, glycerol, propylene glycol or trimethylene glycol.

65. (Currently amended) The method according to claim 64, wherein the polyol in R^4 is derived from glycerol, sorbitol, maltose, trehalose, glucose, sucrose, amylose, pectin, lactose, fructose, dextrose ort dextran.

66. (Original) The method according to claim 65, wherein the polyol in R^4 is derived from glycerol, sorbitol, glucose, maltose or dextran.

67. (Original) The method according to claim 66, wherein the polyol in R^4 is derived from glucose or maltose.

68. (Previously amended) The method according to claim 62 wherein the one or more additives is GluconamideSi (Compound **1**) and/or MaltonamideSi (Compound **2**).

69. (Original) The method according to claim 62, wherein the protein is a kinase, luciferase, or urease or is Factor Xa.

70. (Original) The method according to claim 69, wherein the protein is Src protein tyrosine kinase.

71. (Original) The method according to claim 62, further comprising combining the organic polyol silane precursor and one or more additives with a substrate for the protein to be entrapped.

72. (Original) The method according to claim 71, wherein the protein is a kinase and the substrate is a source of phosphate.

73. (Original) The method according to claim 72, wherein the substrate is ATP.

74. (Previously added) The method according to claim 59, wherein the substance which provides cationic sites that counterbalance an anionic charge of the silica to reduce non-selective interactions is aminopropyltriethoxysilane (APTES), PAM, PPG-NH_2 and/or PEG-NH_2.

75. (New) The method according to claim 39, wherein OR^1, OR^2 and OR^3 are the same or different and are derived from organic di- or polyols.

76. (New) The method according to claim 75, wherein OR^1, OR^2 and OR^3 are the same or different and are derived from sugar alcohols, sugar acids, saccharides, oligosaccharides or polysaccharides.

77. (New) The method according to claim 75, wherein OR^1, OR^2 and OR^3 are the same or different and are derived from allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose, threose, erythrose, glyceraldehydes, sorbose, fructose, dextrose, levulose, sorbitol, sucrose, maltose, cellobiose, lactose, dextran (500-50,000 MW), amylose, pectin, glycerol, propylene glycol or trimethylene glycol.

78. (New) The method according to claim 77, wherein OR^1, OR^2 and OR^3 are the same or different and are derived from glycerol, sorbitol, maltose, trehalose, glucose, sucrose, amylose, pectin, lactose, fructose, dextrose and dextran.

79. (New) The method according to claim 77, wherein OR^1, OR^2 and OR^3 are the same or different and are derived from glycerol, sorbitol, maltose or dextran.

80. (New) The method according to claim 39, wherein OR^1, OR^2 and OR^3 are the same or different and are selected from C_{1-4}alkoxy, aryloxy and arylalkyleneoxy.

81. (New) The method according to claim 80, wherein wherein OR^1, OR^2 and OR^3 are the same or different and are selected from C_{1-4}alkoxy, phenyoxy, naphthyloxy and benzyloxy.

82. (New) The method according to claim 81, wherein wherein OR^1, OR^2 and OR^3 are the same or different and are selected from C_{1-4}alkoxy.

83. (New) The method according to claim 82, wherein OR^1, OR^2 and OR^3 are all ethoxy.

84. (New) The method according to claim 39, wherein R^4 is selected from the group consisting of:

polyol-(linker)-;

polymer-(linker)$_n$-; and

$$R^2O-\underset{OR^3}{\overset{OR^1}{\underset{|}{\overset{|}{Si}}}}-(\text{linker})_n-\text{polymer}-(\text{linker})_n-,$$

wherein n is 0-1.

85. (New) The method according to claim 84, wherein the polyol is an organic di- or polyol.

86. (New) The method according to claim 85, wherein the polyol is selected from the group consisting of a sugar alcohol, sugar acid, saccharide, oligosaccharide and polysaccharide.

87. (New) The method according to claim 86, wherein the polyol is a selected from the group consisting of allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose, threose, erythrose, glyceraldehydes, sorbose,

fructose, dextrose, levulose, sorbitol, sucrose, maltose, cellobiose, lactose, dextran, (500-50,000 MW), amylose, pectin, glycerol, propylene glycol and trimethylene glycol.

88. (New) The method according to claim 87, wherein the polyol is selected from the group consisting of glycerol, sorbitol, maltose, trehalose, glucose, sucrose, amylose, pectin, lactose, fructose, dextrose and dextran.

89. (New) The method according to claim 88, wherein the polyol is selected from the group consisting of glycerol, sorbitol, glucose, maltose and dextrose.

90. (New) The method according to claim 84 wherein the polymer is a water soluble polymer.

91. (New) The method according to claim 90, wherein the polymer is selected from the group consisting of polyethylene oxide (PEO), polyethylene glycol (PEG), amino-terminated polyethylene oxide (PEO-NH_2), amino-terminated polyethylene glycol (PEG-NH_2), polypropylene glycol (PPG), polypropylene oxide (PPO), polypropylene glycol bis(2-amino-propyl ether) (PPG-NH_2), polyvinyl alcohol, poly(acrylic acid), poly(vinyl pyridine), poly(N-isopropylacrylamide) (polyNIPAM) and polyallylamine (PAM).

92. (New) The method according to claim 91, wherein the water soluble polymer is selected from the group consisting of PEO, PEO-NH_2, PEG, PPG-NH_2, polyNIPAM and PAM.

93. (New) The method according to claim 92, wherein the polymer is PEO.

94. (New) The method according to claim 84, wherein the linker is selected from the group consisting of C_{1-20}alkylene, C_{1-20}alkenylene, organic ethers, thioethers, amines, esters, amides, urethanes, carbonates and ureas.

95. (New) The method according to claim 84, wherein the compound of Formula I is selected from one or more of:

GluconamideSi (Compound **1**);

MaltonamideSi (Compound **2**);

DextronamideSi (Compound **3**);

$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~4-5, average MW 200 (Compound **5a**);

$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~13, average MW 600 (Compound **5b**);

$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~44, average MW 2000 (Compound **5c**); and

$(CH_2CH_2O)_p[(EtO)_3Si(C_3H_6)]_2$, p ~227, average MW 10,000 (Compound **5d**).

96. (New) The method according to claim 1, further comprising combining the organic polyol silane and one or more additives in the presence of one or more biomolecules.

97. (New) The method according to claim 39, further comprising combining the organic polyol silane and one or more additives in the presence of one or more biomolecules.

98. (New) The method according to claim 41, further comprising combining the organic polyol silane and one or more additives in the presence of one or more biomolecules.

100. (New) A method for the quantitative or qualitative detection of a test substance that reacts with, binds to and/or whose reactivity is catalyzed by an active biological substance, wherein said biological substance is encapsulated within a siliceous material, comprising:

(a) preparing the siliceous material comprising said active biological substance entrapped within a porous, silica matrix using a method according to claim 98;

(b) bringing said biological-substance-containing siliceous material into contact with a gas or aqueous solution comprising the test substance; and

(c) quantitatively or qualitatively detecting, observing or measuring the change in one or more characteristics in the biological substance entrapped within the siliceous material and/or, alternatively, quantitatively or qualitatively detecting, observing or measuring the change in one or more characteristics in the test substance.

101. (New) The method according to claim 100, wherein the change in one or more characteristics of the entrapped biological substance is qualitatively or quantitatively measured by spectroscopy, utilizing one or more techniques selected from UV, IR, visible light, fluorescence, luminescence, absorption, emission, excitation and reflection.

102. (New) A method of storing a biologically active biological substance in a silica matrix, wherein the biological substance is an active protein or active protein fragment, wherein the silica matrix prepared using a method according to claim 98.